SEKINE

Investigation of Pressure-Temperature Relations of Saturated Sulphur Dioxide & Carbon Dioxide

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INVESTIGATION OF PRESSURE-TEMPERATURE RELATIONS OF SATURATED SULPHUR DIOXIDE AND CARBON DIOXIDE

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Sentaro Sekine

ENTITLED Investigation of Pressure-Temperature Relations of Saturated Sulphur Dioxide and Carbon Dioxide

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Mechanical Engineering

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INVESTIGATION OF PRESSURE-TEMPERATURE RELATIONS OF SULPHUR DIOXIDE AND CARBON DIOXIDE

I. INTRODUCTION

SULPHUR dioxide and Carbon dioxide, as refrigerating media are excelled in certain respects by Ammonia; nevertheless they have some characteristic advantages and are employed extensively in small refrigerating plants and cold storage installations. The use of these media faciliated by the introduction of electric motors, is increasing rapidly in refrigerating industry.

Scientists and engineers have already investigated the physical properties of these fluids and the results are published; and refrigrating engineers await for the result of the further investigation of the property derived from the known experimental results.

The purpose of the present investigation is to derive one of the important relations, namely the relation between the pressure and temperature of the saturated vapors.

II. LAWS GOVERNING VAPOR PRESSURES

(a) Ramsay and Young's Law

A general law for the temperatures of any two substances under the same vapor pressure, was announced by Ramsay and Young.[1] The law, as now given is expressed by the equation,

$$\frac{T_a}{T_b} = \frac{T_a'}{T_b'} + k(T_a - T_a'),$$

where T_a and T_b are the absolute temperatures of any two substances corresponding to a given pressure p, T_a' and T_b' the absolute temperatures of the substances corresponding to any other vapor pressure p', and k aconstant for a pair of substances.

This relation was verified for twenty-three pairs of substances by Ramsay and Young, and for other substances by several other investigators.

(b) Method of Computing Vapor-pressure

Ramsay and Young stated that by means of the relation $T_a/T_b = T_a'/T_b' + k(T_a - T_a')$, vapor-pressures of any substance can be computed, if two, or better, more temperatures of the substance and the pressure-temperature relations of any other substance are accurately known. On this principle, the vapor-pressure of oxygen and of other substances were computed and found to agree closely with observed data. The explanation of this method applied in computing the vapor-pressures of krypton is fully given by Travers.[2]

Suppose we have obtained the following data (values in first two columns)and are required to find the vapor-pressures of krypton.

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* The numerals on the right shoulder of words refer to BIBLIOGRAPHY

Pressure	T_{kr}	T_{aq}	T_{kr}/T_{aq}
386.6	112.7	355.1	0.3174
898.7	123.1	377.5	.3264
11970.	170.9	474.3	.3603
[illegible]3808.	197.9	5[illegible]1.2	.3797
3[illegible]837.	201.0	5[illegible]5.1	.3828
31621.	201.5	526.0	.3826
34693.	204.1	532.[illegible]	.3835
37006.	206.4	536.2	.3849
41245.	210.5	544.3	.3870

First, calculate values of T_{kr}/T_{aq} as shown above. Plot points on a coordinate system, the temperature of water as ordinates and the corresponding values of T_{kr}/T_{aq} as abscissae; and draw a straight line that passes through most of the points plotted. Now in order to find the absolute temperature corresponding to a given pressure of krypton, find the absolute temperature of water corresponding ~~to~~ to the same pressure and from the diagram get the value of T_{kr}/T_{aq} corresponding to the temperature. Then the product of the value of T_{kr}/T_{aq} is found and the absolute temperature of water will give the absolute temperature of krypton corresponding to the given pressure. Repeat for other pressures and plot on a diagram the pressure-temperature relations of krypton. On this diagram, now, the vapor-pressure of krypton corrsponding to any temperature may be read directly.

(c) Moss's Expression of Ramsay and Young's law

Prof. Sanford A. Moss has reduced Ramsay and Young's law to a simple form, thus:

$$\frac{T_a}{T_b} = \frac{T'_a}{T'_b} + k(T_a - T'_b) \qquad T'_a$$

$$\frac{1}{T_b} = \frac{1}{T_a}\frac{T'_a}{T'_b} + k - \frac{1}{T_a}kT'_a$$

$$= \frac{1}{T_a}\left(\frac{T_a'}{T_b'} - kT_a'\right) + k,$$

But, since T_a' and T_b' are the absolute temperatures of two substances, corresponding to some particular vapor-pressure, the coefficient of $1/T_a$ is evidently a constant, say c. Then we have,

$$\frac{1}{T_b} = c\frac{1}{T_a} + k$$

Here T_a and T_b are absolute temperatures of any two substances under the same vapor-pressure, and c and k are constants for each pair of substances. This is a very simple, if not the simplest, expression of Ramsay and Young's law, and has remarkable advantages in computation of vapor-pressures and in graphical representation of the law.

(d) Graphical Representation of Ramsay and Young's Law

The discussion of graphical representation of Ramsay and Young's law is given by Moss[3]. Suppose it is required to find the temperature-pressure relation of any substance from that of water vapor, which is already determined accurately. Then the law may be conventionally expressed as

$$\frac{1}{T_z} = c\frac{1}{T_w} + k$$

or $$-x = -cy + k,$$

in which $x = -1/T_z$ and $y = -1/T_w$. Since y is a function of the water vapor temperature T_w, and T_w is a function of the corresponding pressure p, ($\log p = B - A/T_w - CT_w + DT_w^2$), y is also a function of p. x is a function of the temperature T_z corresponding to this same pressure p. The equation may, therefore, be written as

$$-f(T_z) = -cF(p) + k$$

This is an equation representing the pressure-temperature relation of any substance z.

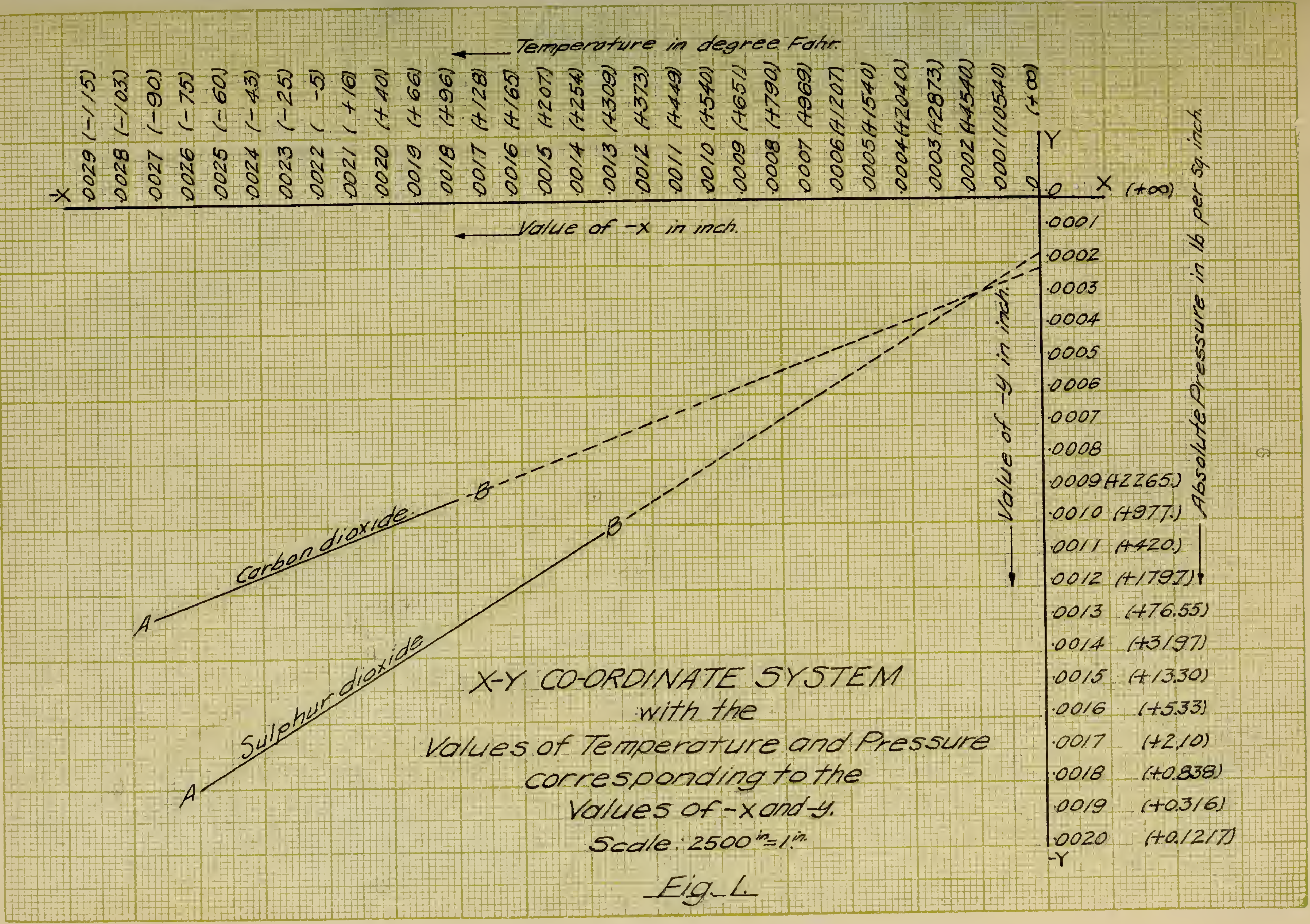
Now, if we represent the equation $-x = -cy + k$ on a plane with x-y coordinates, it is evidently a straight line. This is shown by the lines AB on fig. 1. Hence values of ~~of~~ y corresponding to any value of x may be found on the diagram.

Since, however, $x = f(T_z)$ and $y = F(p)$, we may label the values of x and y with the respective values of T_z and p which they represent, as shown by the figures in the parentheses on Fig. 1. Then we can read directly pressures of any substance z corresponding to assumed temperatures.

Since the same formula with different constants applies to any substance, the x and y axes may be labeled without regard to any particular vapor. The values of x and y corresponding to the values of temperatures and pressures, however, must be calculated according to the assumptions; that is $x = f(T_z) = -1/T$, and $y = \phi(T_w) = F(p)$. The method of the construction of this diagram for a practical purpose will be shown in (a)IV.

When the values are labeled on the axes, plot all the known points of any substance and draw the straight line that best represents the points. Then the vapor pressure corresponding to any temperatures of the substance can be read directly on the diagram.

The advantages of this diagrams are; (1) since the curve representing the pressure-temperature relation of any substance is a straight line on this diagram, the continuous curve best representing the observed points of any vapor can be determined most easily by means of this diagram, (2) when the curve of a substance is shown



X-Y CO-ORDINATE SYSTEM
with the
Values of Temperature and Pressure
corresponding to the
Values of −x and −y.
Scale: 2500 in = 1 in.

Fig. L

the pressure of that substance corresponding to any assumed temperature can be read directly on this diagram, (3) the more accurate values of pressure and temperature can be computed, when the constants of the equation $1/T_Z = c(1/T_W)+k$ are determined by means of the diagram.

(e) Marks's Equation for the Pressure-Temperature Relation of Saturated Steam

From Van der Waals' equation for vapors, Prof. Lionel S. Marks has derived a pressure-temperature equation for saturated water vapor.[*]

Van der Waals gives for vapors the following equation.

$$\log\frac{p_c}{p} = a\left(\frac{T_c}{T}-1\right)$$

where p_c and T_c are the critical constants, p the absolute saturation pressure corresponding to any absolute temperature T, and a a constant.

Nernst gives a diagram of the values of $\left(\frac{T_c}{T}-1\right)$ plotted against the values of $\log\frac{p_c}{p}$ for nine different substances. The result seem to indicate a straight line relation between $\log\frac{p_c}{p}$ and $\left(\frac{T_c}{T}-1\right)$.

Marks plotted the values of "a" in the Van der Waals' equation against the reduced temperature $\frac{T}{T_c}$, and found that the value of "a" in the Van der Waals' equation is not a constant but assumes the following relation

$$a = b\left\{1+c\frac{T}{T_c}+d\left(\frac{T}{T_c}-0.78\right)^2\right\}.$$

After numerous trials the following equation was found:

$$\log\frac{p_c}{p} = 3.006854\left(\frac{T_c}{T}-1\right)\left\{1+0.0505476\left(\frac{T}{T_c}\right)+0.629547\left(\frac{T}{T_c}-0.7875\right)^2\right\}$$

Inserting the chosen values of critical constants (T_c=706.3+459.64 deg F., p_c=3200. lbs. per squ. in. by Holborn and Baunmann), this reduced to

$$\log p = 10.515354-4873.71T^{-1}-0.00405096T+0.000001392964T^2.$$

The agreement of the pressures calculated from this equation with the experimental results of Holborn and Baunmann is very striking, the maximum difference being about 0.1 of one percent in the range from 212. degrees Farh. to the critical temperature, and o.195 per cent at 50. degrees Fahr. below 212.deg. F.

III. EXPERIMENTAL DATA

(a) Data for Sulphur Dioxide

(1) Renault's experimental data[6]

Temperature deg. Cent.	Pressure m.m.Hg.	Temperature deg. Fahr.	Pressure lbs.per sq. in.
-30.24	318.67	-22.432	6.16
-30.11	318.05	-22.198	6.15
-30.11	318.99	-22.198	6.17
-29.45	324.80	-21.010	6.28
-27.63	325,56	-17.734	6.30
-27.50	328.28	-17.50	6.35
-27.33	331.08	-17.194	6.40
-27.21	332.82	-16.975	6.44
-26.86	337.23	-16.348	6.52
-26.22	348.35	-15.190	6.74
-24.88	394.40	-12.784	7.63
-22.02	444.89	-7.636	8.61
-18.74	501.14	-1.732	[illegible]
-18.52	515.87	-1.376	9.98
-18.25	520.49	-0.850	10.07
-13.48	648.61	7.736	12.55
-13.37	647.12	7.934	12.52
-13.27	654.15	8.114	12.65
-10.55	739.90	13.010	14.31
-10.48	745.50	13.136	14.42
-10.34	745.75	13.388	14.43
-10.31	745.92	13.442	14.43
-8.97	792.46	15.854	15.33
-7.61	842.30	18.302	16.30
-5.76	912.17	21.632	17.64
-5.74	912.33	21.668	17.65
-4.16	979.42	24.512	18.95
0	1164.58	32.	22.53
0	1170.47	32.	22.64
1.35	1228.81	34.43	23.77
1.43	1231.31	34.573	23.82
2.48	1286.57	36.464	24.89
3.56	1338.74	38.408	25.90
4.56	1393.87	40.208	26.96
6.55	1485.30	43,79	28.73
9.54	1698;23	49.172	32.85
9.64	1707.18	49.352	32.02
13.36	1953.17	56.048	37.78
19.70	2454.50	67.450	47.47
20.78	2532.01	69.404	48.97
21.31	2593.10	70.358	50.16
21.35	2594.82	70.430	51.19

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[illegible]9.94	3403.25	85.89[illegible]	65.81
29.95	3403.25	85.91	65.81
30.12	3497.02	86.[illegible]	6[illegible].64
30.22	3495.17	86.396	67.60
37.15	4344.89	98.87	84.04
37.59	4726.89	99.6[illegible]	83.69
39.18	4752.[illegible]7	102.[illegible]	91.93
45.26	5427.30	113.464	104.98
48.66	6195.91	119.58	119.85
49.46	6112.88	121.010	118.40
62.52	8662.18	144.536	167.55

This table contains in English units all the observations of SO_2 in the three series of experiments made by Regnault. In the conversion of m.m.Hg. into lbs. per sq. in., the following relation was adapted:

1000.m.m.Hg.=1.00033x19.337 lbs. per sq. in.

=19.343 lbs. per sq. in.,

or 1. m.m.Hg. = 0.019343 lbs. per sq. in.,

becouse Regnault's experiments were performed at Paris, and the results were not corrected for the standard pressure.

(2) Sajotschewski's experimental data[7]

Temperature deg. Cent.	Pressure Atm.	Temperature deg. Fahr.	Pressure lbs. per sq. in.
50.	8.45	122.	123.9
60.	11.09	140.	163.0
70.	14.31	158.	210.4
80.	18.09	176.	265.9
90.	22.47	194.	330.3
100.	27.82	212.	408.9
110.	33.95	230.	499.0
120.	41.56	248.	610.8
130.	49.97	266.	734.5
140.	60.50	284.	889.3
150.	71.45	302.	1050.3

(3) Blümcke's experimental data[8]

Temperature deg. Cnet.	Pressure Atm.	Temperature deg. Fahr.	Pressure lbs. per sq.in.
-19.5	0.60	-3.1	8.82
-11.5	0.95	11.3	13.97

0.	1.51	32.0	22.20
35.0	5.45	95.0	80.11
46.7	7.55	116.06	110.99
65.0	12.87	149.0	188.60
77.5	17.12	171.5	251.65
98.2	26.96	208.8	396.28

(4) Miller's experimental data[9]

Temperature deg. Fahr.	Pressure lbs.per sq.in.
68.20	49.41
74.80	55.35
81.04	61.77
87.05	68.80
92.22	76.07
98.37	82.56
103.12	89.59
106.20	94.72
109.62	99.77
112.32	104.57
115.05	109.01
124.72	127.75
128.74	133.29
129.95	137.17
131.97	138.70
139.11	154.40
142.86	160.92
144.06	166.45
146.31	173.20
148.65	178.46
151.13	184.59
154.37	193.12
156.63	200.01
158.29	204.80
161.94	215.58
164.29	222.78
166.71	229.21
168.53	236.03
171.00	243.61
172.78	249.65
176.51	262.71
178.97	270.96
180.33	276.78
183.32	287.50
185.01	294.73
186.51	303.26
189.24	311.26
191.29	317.21
192.58	323.64
194.19	330.54
195.23	337.25
197.14	344.70

198.71	352.12
200.01	358.01
201.21	363.80
202.33	368.76
203.05	371.84
204.97	381.18
206.49	388.04
207.24	392.48
208.26	398.08
209.80	405.89
210.41	409.72
211.14	416.74

The preceding table is the summary of the observations by Miller, corrected for the lag and errors in the thermometer and errors in the gage.

(5) Pictet's experimental data[10]

Temperature deg. Cent.	Pressure Atm.	Temperature deg. Fahr.	Pressure lbs.per sq. in.
-30.	0.36	-22.0	5.29
-20.	0.61	-4.0	8.97
-10.	1.00	14.0	14.70
o.	1.51	32.0	22.20
10.	2.35	50.0	34.54
30.	4.60	86.0	67.62
50.	8.30	122.0	122.00

(6) Data for triple point of sulphur dioxide

The triple point of sulpher dioxide is not yet determined accuratetely. the theoretical triple point for sulphur dioxide or for any other substance, may be calculated when the equations of subliming curve and saturated vapor curve of the substance are known.

(7) Critical data of sulphur dioxide

Critical temperature deg. Cent.	Critical pressure Atm.	Critical temperature deg. Fahr..	Critical pressure lbs.per sq.in.	Experimenter
155.4	78.9	279.72	1159.9	Dewar[11]
155.4	----	279.72	----	Sajotschewski[12]
140.0	----	252.0	----	Drion[13]
157.-161.	----	282.6-289.8	----	Van Ladenburg[14]

(b) Data for Carbon Dioxide

(1) Amagat's experimental data[24]

Temperature deg.Cent.	Pressure Atm.	Temperature deg.Fahr.	Pressure lbs.per sq.in.
0.	34.3	32.	504.2
1.	35.2	33.8	517.4
2.	36.1	35.6	530.6
3.	37.0	37.4	543.8
4.	38.0	39.2	558.5
5.	39.0	41.0	573.3
6.	40.0	42.8	587.9
7.	41.0	44.6	602.5
8.	42.0	46.4	617.2
9.	43.1	48.2	633.0
10.	44.2	50.0	649,7
11.	45.3	51.8	665.9
12.	46.4	53.6	682,0
13.	47.5	55.4	698.2
14.	48.7	57.2	715.9
15.	50.0	59.0	735.0
16.	51.2	60.8	752.5
17.	52.4	62.6	770.1
18.	53.8	64.4	790.8
19.	55.0	66.2	808.5
20.	56.3	68.0	823.2
21.	57.6	69.8	846.7
22.	59.0	71.6	867.3
23.	60.4	73.4	887.9
24.	61.8	75.2	908.4
25.	63.3	77.0	930.5
26.	64.7	78.8	951.0
27.	66.2	80.6	973.1
28.	67.7	82.4	995.2
29.	69.2	84.2	1017.2
30.	70.7	86.0	1039.3
30.5	71.5	86.9	1051.1
31.0	72.3	87.8	1062.8
31.25	72.8	88.25	1070.2
31.35	72.9	88.43	1071.6

Amagat's observed data for CO_2 are given only in the form of a diagram. The table given by Amagat and shown above contains in part smoothed values. It may be taken, however, as representing his experimental data, because smooth curve passes exactly through all his observed points plotted on his diagram.

(2) Andrews' experimental data[25]

Temperature deg.Cent.	Pressure Atm.	Temperature deg.Fahr.	Pressure lbs.per sq.in.
0	35.04	32.	515.0
5.45	40.44	41.81	594.3
11.45	47.04	52.61	691.4
16.92	53.76	62.46	790.2
22.22	61.13	71.99	898.6
25.39	65.79	77.68	967.1
28.30	70.37	82.94	1034.5

(3) Cailletet's experimental data[26]

Temperature deg.Cent.	Pressure Atm.	Temperature deg.Fahr.	Pressure lbs.per sq.in.
-50.	6.83	-58.	100.40
-40.	10.25	-40.	150.67
-34.	12.70	-29.2	186.70

(4) Kuenen and Robson's experimental data[27]

Temperature deg.Cent.	Pressure Atm.	Temperature deg.Fahr.	Pressure lbs.per sq.in.
0	34.34	32.	504.80
-9.95	26.04	14.17	382.75
-9.95	25.99	14.17	382.00
-15.27	22.23	4.51	326.80
-21.67	18.32	-7.00	269.30
-27.01	15.42	-16.61	226.67
-32.88	12.60	-27.18	185.22
-33.08	12.59	-27.54	185.08
-41.02	9.46	-41.82	139.07
-47.58	7.34	-53.64	107.90
-54.52	5.45	-66.14	80.12
-54.68	5.45	-66.44	80.12
-56.18	5.10	-69.12	74.96
-56.24	5.10	-69.23	74.96

(5) Stähli's experimental data[28]

Temperature deg.Cent.	Pressure m.Hg.	Temperature deg.Fahr.	Pressure lbs.per sq.in.
-10.	19.63	14.00	379.5
-20.	14.83	-4.00	286.7
-30.	10.80	-22.00	208.8

-40.	7.51	-40.00	145.2
-50.	5.12	-58.00	98.97
-56.4	3.91	-69.52	75.59

(6) Zelney's experimental data[29]

Temperature deg.Cent.	Pressure Atm.	Temperature deg.Fahr.	Pressure lbs.per sq.in.
-3.7	30.04	25.34	441.7
-4.5	29.47	23.90	433.2
-12.3	24.016	9.86	353.0
-14.2	23.150	6.44	340.3
-22.4	18.153	-8.32	266.9
-26.15	16.184	-15.07	237.9
-31.6	13.45	-22.88	197.7
-32.65	13.002	-26.77	191.1
-40.1	9.847	-40.18	144.8
-41.9	9.195	-43.42	135.2
-44.0	8.535	-47.20	125.5
-46.1	7.834	-50.98	115.2
-46.75	7.32	-52.15	107.6
-51.25	6.371	-60.25	93.66
-53.0	5.959	-63.4	87.60
-54.3	5.6	-65.74	82.32
-54.7	5.446	-66.46	80.06
-54.8	5.355	-66.64	78.72
-55.4	5.322	-67.72	78.24
-55.45	5.34	-67.81	78.50
-55.45	5.368	-67.81	78.91
-56.05	5.226	-68.89	76.83
-56.20	5.207	-69.16	76.55

(7) Data for triple point of CO_2

Temperature deg.Cent.	Pressure	Temperature deg.Fahr.	Pressure lbs.per sq.in.	Experimenter
-56.4	3.91 m.Hg.	-69.52	75.59	Stählì[28]
-56.24	5.10 Atm.	-69.232	74.96	Kuenen & Robson[27]
------	5.112 Atm.	-----	74.98	Zelney[29]

(8) Data for critical point of CO_2

Critical temperature deg.Cent.	Critical pressure Atm.	Critical temperature deg. Fahr.	Critical pressure lbs.per sq.in.	Experimenter
31.35	72.9	88.74	1071.6	Amagat[24]
30.92	77.0	87.656	1131.9	------[30]

IV. DERIVATION OF PRESSURE-TEMPERATURE EQUATIONS

(a) Construction of Diagram

Since the pressure-temperature relation of saturated steam has been so accurately determined, the investigation of the said relations of other substances are very conveniently made by plotting the experimental data on the diagram constructed by Moss's method. The diagram shown on Fig.2 was deviced on this basis.

This diagram represents with larger scale only the part of the diagram on Fig.1, necessary for the investigation of Sulphur dioxide and Carbon dioxide. the actual values of x and y which, in fact, only necessary for the explanation of the diagram, are not here shown; but they are replaced with the corresponding values of the temperature in degree Fahr. and the pressure in pound per square inch. To do this, however, the values of x and y correspoinding to the integral numbers of the temperatureand the pressure must be calculated. Some of the computations are shown as follows:[31]

Abscissae

Fahrenheit Temperature	Absolute Temperature	Reciprocal of Absolute Temperature or Value of x	Corresponding Values Of x' in Inches refered to the point -10. as Origin $=-(8000(1/T)-10.)$
-100.	359,64	0.0027806	-12.244
-50.	409.64	0.0024412	-9.529
0	459.64	0.0021756	-7.405
50.	509.64	0.0019622	-5.697
100.	559.64	0.0017869	-4.295
150.	609.64	0.0016403	-3.122
200.	659,64	0.0015160	-2.128
250.	709.64	0.0014092	-1.273

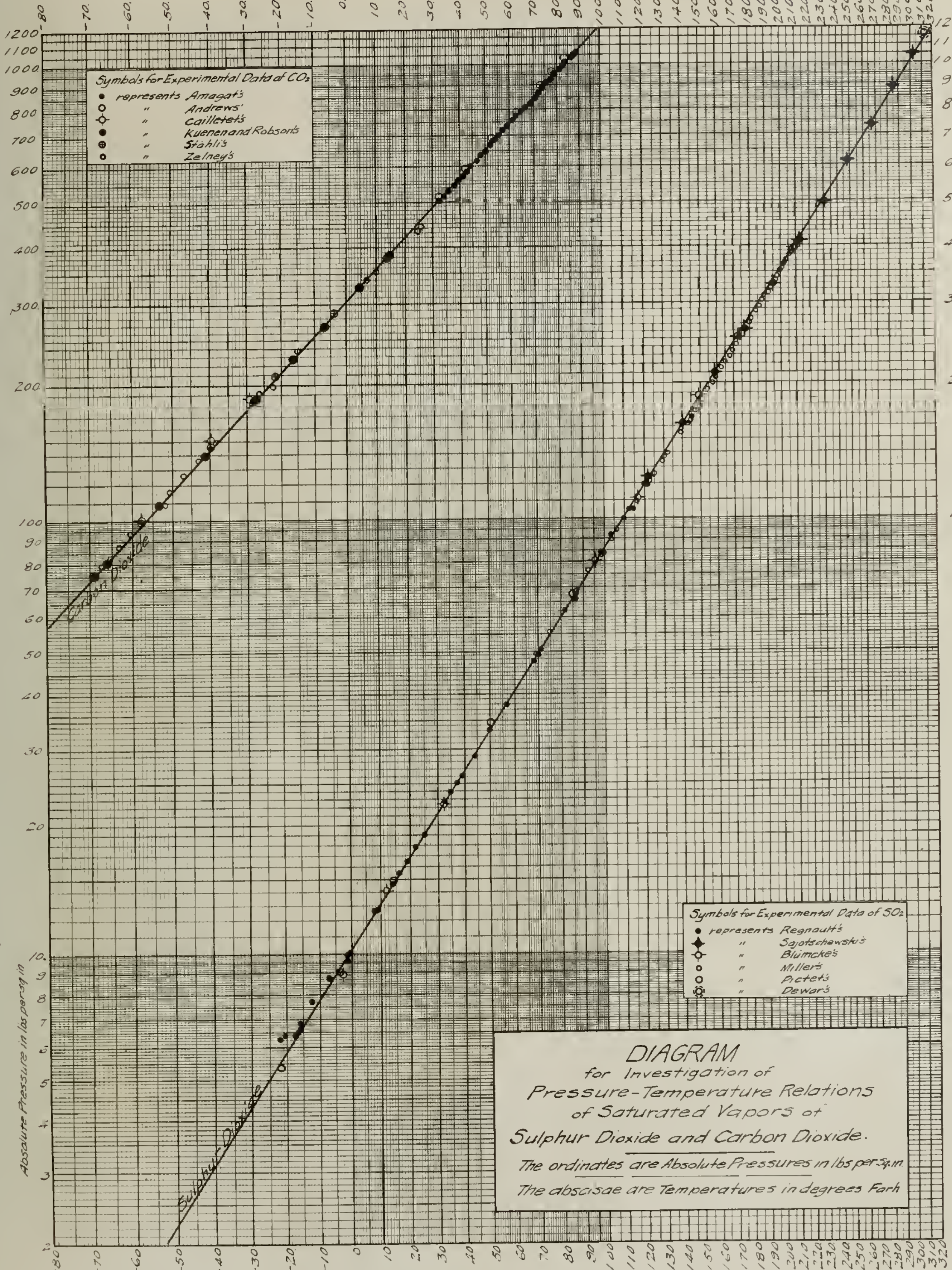

Fig. 2.

June 7, 1912 S Sekine

Ordinates

Pressure lbs per sq.in.	Cprresponding Saturation Temperature of Water Vapor in Degree Fahr.	Absolute Temperature	Reciprocal of Absolute Temperature or Value Of x	Corresponding Values of y' in Inches refered to the Point -18. as Origin =-(20000(1/T)-18)
1.	101.83	561.47	0.0017810	-17.621
5.	162.28	621.92	0.0016079	-14.158
10.	193.22	652.86	0.0015371	-12.634
50.	281.22	740.64	0.0013502	-9.004
100.	327.8	787.44	0.0012699	-7.399
500.	467.2	926.84	0.0010789	-3.579
1000.	544.9	1004.54	0.0009955	-1.910
1700.	613.4	1073.04	0.0009319	-0.639

The values of x' and y' have been, as shown on the last columns of the preceding tables, also calculated in order to construct the diagram with a scale convenient for the present purpose. It will be noticed that the new origin was located at the point (-10",-18") of the x'y' coordinate system, Or at (-0.000125,-0.0009) of the x-y coordinate system.

The experimental data were all plotted and each set of the experimental results was represented by a particular symbol. The straight lines "Sulphur Dioxide" and "Carbon Dioxide" were located at such positions that they represent the most probable pressure-temperature relations of saturated vapors of sulphur dioxide and carbon dioxide.

By means of this diagram, we are now able to read directly the saturated vapor pressures of the substances cOrresponding to any temperature within the limit of the diagram; and also to calculate more accurate values of the pressure, when the constants of the equation $1/T_W = c(1/T)+k$ are determined by means of the diagram and the steam table.

(b) Determination of the Constants c and k for Sulphur Dioxide and for Carbon Dioxide

To solve for the values of the constants in the expression $1/T_w = c(1/T_{so_2}) + k$, the following pressure-temperature relations of SO_2 have been taken from the diagram.

Point	Pressure in Lbs per Square Inch	Saturated Vapor of Sulphur Dioxide: Temp. in Deg. F.	Absolute Temp. in Deg. F., $=T_{so_2}$	$1/T_{so_2}$	$\text{Log}(1/T_{so_2})$	Saturated Steam: Absolute Temp. in Deg. F., $=T_w$	$1/T_w$
1	2.	-53.2	406.44	.00246039	$\bar{3}$.3910036	585.79	.00170709
2	3.	-41.3	418.34	.00239040	$\bar{3}$.3784706	601.16	.00166341
3	5.	-25.15	434.49	.00230155	$\bar{3}$.3620202	621.92	.00160792
4	500.	228.5	688.14	.00145319	$\bar{3}$.1623232	926.84	.00107893
5	800.	274.5	734.14	.00136214	$\bar{3}$.1342211	978.14	.00102235
6	1200.	319.0	778.64	.00128429	$\bar{3}$.1086633	1027.04	.00097367

To determine the value of the constant c at first, the simultaneous equations $1/T'_w = c(1/T'_{so_2}) + k$ and $1/T''_w = c(1/T''_{so_2}) + k$ may be transformed as follows:

$$\frac{1}{T'_w} = c\frac{1}{T'_{so_2}} + k \qquad \text{-------------------------(1)}$$

$$\frac{1}{T''_w} = c\frac{1}{T''_{so_2}} + k \qquad \text{-------------------------(2)}$$

subtracting (1) from (2) we have,

$$\frac{1}{T''_w} - \frac{1}{T'_w} = c\left(\frac{1}{T''_{so_2}} - \frac{1}{T'_{so_2}}\right)$$

$$c = \frac{\dfrac{1}{T''_w} - \dfrac{1}{T'_w}}{\dfrac{1}{T''_{so_2}} - \dfrac{1}{T'_{so_2}}},$$

in which T'_w and T'_{so_2} are the absolute temperatures of the saturated steam and the saturated sulphur dioxide under the same prssure, T''_w and T''_{so_2} the absolute temperatures of the substances under any other pressure, and c the particular constant for this pair of the substances. Now, substituting the values of the points "1" and "4" in the equation (3), we we get

$$c = \frac{\frac{1}{T''_w} - \frac{1}{T'_w}}{\frac{1}{T''_{so_2}} - \frac{1}{T'_{so_2}}} = \frac{.00170709 - .00107893}{.00256039 - .00145319} = \frac{.00062816}{.00100720} = 0.623645,$$

4

with the points "1" and "5", we get

$$c = \frac{.00068474}{.00109825} = 0.623483,$$

from "1" and "6"

$c = 0.623604,$

from "2" and "4"

$c = 0.623638,$

from "2" and "5"

$c = 0.623442,$

from "2" and "6"

$c = 0.623573,$

from "3" and "4"

$c = 0.623544,$

from "3" and "5"

$c = 0.623338,$

and from "3" and "6"

$c = 0.623488.$

The avarage value of the nine values of c was found as 0.623528; and the value 0.62353 has been adapted as the value of c for the pair of SO_2 and Steam.

Taking the value of c as 0.62353, the value of the constant k was enumerated as follows:

Using values of the point "1," we get,

$$\frac{1}{T'_w} = c\frac{1}{T'_{SO_2}} + k$$

$$k = \frac{1}{T'_W} - c\frac{1}{T'_{SO_2}}$$

$$= 0.00170709 - \frac{0.62353}{406.44}$$

$$= 0.00170709 - 0.00153412$$

$$= 0.00017297.$$

With the values of the point "2", we get,

$$k = 0.00166341 - \frac{0.62353}{418.34}$$

$$= 0.00166341 - 0.00149049$$

$$= 0.00017292,$$

from "3" $k = 0.00017284,$

from "4" $k = 0.00017282,$

from "5" $k = 0.000173006$

and from "6" $k = 0.000172876.$

The avarage of these six values of k was found as 0.00017290.

Therefore, the relation between the absolute temperature of saturated steam and saturated vapor of sulphur dioxide under the same vapor pressure is now expressed as

$$\frac{1}{T_w} = 0.62353\frac{1}{T_{SO_2}} + 0.0001729 \quad \text{---------- ----------(I)}$$

This formula has been tested for many points on the curve of SO_2 on the diagram, and found to agree very closely.

In a similar manner, the constants c and k of the expression $1/T_W = c(1/T_{CO_2}) + k$ for the pair of saturated vapors of carbon dioxide and water have been determined. Namely

$$\frac{1}{T_W} = 0.42909\frac{1}{T_{CO_2}} + 0.00020433. \text{------ ------------(II)}$$

This formula also has been tested, and found to represent the curve for carbon dioxide on the diagram.

These formulae enable one to find the vapor pressure of the sulphur dioxide and of the carbon dioxide corresponding to any temperature with the aid of the steam table. Suppose, for instance, the vapor pressure of saturated carbon dioxide at the temperature of 50. deg. F. is required. We have

$$\frac{1}{T_W} = 0.42907\frac{1}{459.64+50} + 0.00020433$$

$$= \frac{0.42907}{509.64} + 0.00020433$$

$$= 0.00084254 + 0.00020433$$

$$= 0.00104687$$

$T_W = 955.23$ deg. F. abs. $= 495.59$ deg. F.

On Marks and Davis' Steam Table, the vapor pressures corresponding to 490.deg. and 500.deg, are given as 622. and 682. lbs per sq. in. abs. Hence, by a straight line relation, the pressure corresponding to 495.59 deg.F. is found as 656.6 lbs per sq. in. abs. Since the two substances are under thr same pressure, the vapor pressure of saturated carbon dioxide at the temperature 50.deg.F. must be 656.6 lbs per sq. in. absolute.

(c) Derivation of a General Formula for Pressure-Temperature Relation

Combining Marks' general formula for the pressure-temperature relations of saturated steam and Ramsay and Young's law, ~~ew~~ we get a general formula for vapors, thus:

$$\log p = A - \frac{B}{T_w} - CT_w + DT_w^2, \qquad \frac{1}{T_w} = c\frac{1}{T_z} + k$$

$$= A - B\left(\frac{c}{T_z} + k\right) - C\left(\frac{T_z}{c+kT_z}\right) + D\left(\frac{T_z}{c+kT_z}\right)^2$$

$$= A - \frac{Bc}{T_z} - Bk - \frac{C}{k}\left(\frac{T_z}{\frac{c}{k}+T_z}\right) + \frac{D}{k^2}\left(\frac{T_z}{\frac{c}{k}+T_z}\right)^2$$

Let $A' = (A - Bk)$, $B' = Bc$, $C' = C/k$, $D' = D/k^2$ and $c' = c/k$, then

$$\log p = A' - \frac{B'}{T_z} - C'\left(\frac{T_z}{c'+T_z}\right) + D'\left(\frac{T_z}{c'+T_z}\right)^2$$

$$= A' - \frac{B'}{T_z} - C'\left(1 - \frac{c'}{c'+T_z}\right) + D'\left(1 - \frac{c'}{c'+T_z}\right)^2$$

$$= A' - \frac{B'}{T_z} - C'\left(1 - \frac{c'}{c'+T_z}\right) + D'\left(1 - \frac{2c'}{c'+T_z} + \left(\frac{c'}{c'+T_z}\right)^2\right)$$

$$= A' - \frac{B'}{T_z} - C' + \frac{C'c'}{c'+T_z} + D' - \frac{2c'D'}{c'+T_z} + D'\left(\frac{c'}{c'+T_z}\right)^2$$

Let $A'' = (A' - C' + D')$ and $C'' = (C' - 2D')$, then

$$\log p = A'' - \frac{B'}{T_z} + C''\left(\frac{c'}{c'+T_z}\right) + \left(\frac{c'}{c'+T_z}\right)^2 D'$$

Let $-C''' = c'C''$ and $D'' = (c')^2 D'$, then

$$\log p = A'' - \frac{B'}{T_z} - \frac{C'''}{(c'+T_z)} - \frac{D''}{(c'+T_z)^2} \qquad \text{-------------------(III)}$$

But, by the assumption,

$$A'' = A' - C' + D' = A - Bk - C/k + D/k^2,$$

$B' = Bc,$

$$C''' = -c'C'' = -(c/k)(C'-2D') = -\frac{c}{k}\left(\frac{C}{k} - \frac{2D}{k^2}\right) = \left(\frac{2cD}{k^3} - \frac{cD}{k^2}\right),$$

$$D'' = (c')^2 D' = \left(\frac{c}{k}\right)^2 \frac{D}{k^2} = \frac{c^2 D}{k^4},$$

$$c' = \frac{c}{k},$$

therefore,

$$\log p = \left(A - Bk - \frac{C}{k} + \frac{D}{k^2}\right) - \frac{Bc}{T_z} - \frac{\left(\frac{2cD}{k^3} - \frac{cC}{k^2}\right)}{\frac{c}{k} + T_z} - \frac{\left(\frac{c^2 D}{k^4}\right)}{\left(\frac{c}{k} + T_z\right)^2}, \quad \text{---(III')}$$

where T_z is the absolute temperature of any substance z corresponding to vapor pressure p, c and k the constants in the equation $1/T_w = c/T_z + k$ for the pair of saturated steam and any substance z, and other constants have the following values:

$A = 10.515354$

$B = 4873.71$

$C = 0.00405090$

$D = 0.000001392964$

This is the general formula of pressure-temperature relation for vapors. When the constants c and k of the pair of saturated steam and a given substance are determined, this general formula is reduced to the pressure-temperature equation of that particular substance.

(d) Derivation of a General Expression for the Derivative $\frac{dp}{dt}$.

From the general formula derived in the preceding article, the general expression of the derivative for vapors is derived, thus:

$$\log p = A'' - \frac{B'}{T_z} - \frac{C'''}{c' + T_z} + \frac{D''}{(c' + T_z)^2}$$

$$m\frac{dp}{p} = -\frac{-B'dt}{T_z^2} - \frac{-C'''dt}{(c'+T_z)^2} + \frac{-D''(c'+T_z)dt}{(c'+T_z)^4}$$

$$= \left(\frac{B'}{T_z^2}dt + \frac{C'''}{(c'+T_z)^2}dt - \frac{D''}{(c'+T_z)^3}dt\right)2.3026$$

$$\frac{dp}{dt} = 2.3026p\left(\frac{B'}{T_z^2} + \frac{C'''}{(c'+T_z)^2} - \frac{D''}{(c'+T_z)^3}\right)$$

But, $B'=Bc$, $C'''=\left(\frac{2cD}{k^3} - \frac{cC}{k^2}\right)$, $D''=\frac{c^2D}{k^4}$, and $c'=\frac{c}{k}$, therefore,

$$\frac{dp}{dt} = 2.3026p\left(\frac{Bc}{T_z^2} + \frac{\left(\frac{2cD}{k^3} - \frac{cC}{k^2}\right)}{\left(\frac{c}{k} + T_z\right)^2} - \frac{\frac{c^2D}{k^4}}{\left(\frac{c}{k} + T_z\right)^3}\right) \text{-------(IV).}$$

(c) Derivation of the Pressure-Temperature Formulas for Sulphur Dioxide and Carbon Dioxide

The formula for the pressure-temperature relation of sulphur dioxide has been derived by substituting the values of c and k in the general formula for vapors, thus:

Now, $c=0.62353$

$k=0.0001729$

$A=10.515354$

$B=4873.71$

$C=0.00405096$

$D=0.00001392964$, therefore,

$$A''=A-Bk-\frac{C}{k}+\frac{D}{k^2} = 10.515354-4873.71\times0.0001729-\frac{0.00405096}{0.0001729}$$

$$+\frac{0.00001392964}{(0.0001729)^2},$$

$=10.515354-0.842664-23.429492+3[illegible].849348$

$=32.838830,$

$B'=Bc=4873.71 \times 0.0001729$

$=3038.904,$

$$C'''=\left(\frac{2cD}{k^3}-\frac{cC}{k^2}\right)=\frac{2\times 0.62353\times 0.000001392964}{(0.0001729)^3}-\frac{0.62353\times 0.0040509 6}{(0.0001729)^2}$$

$=336079.82 - 84494.08$

$=251585.74,$

$$D''=\frac{c^2D}{k^4}=\frac{(0.62353)^2\times 0.000001392964}{(0.0001729)^4}$$

$=606003055.,$

$$c'=\frac{c}{k}=\frac{0.62353}{0.0001729}$$

$=3606.303.$

Therefore, the pressure-temperature relation of SO_2 is expressed as follows:

$$\log p = 32.83887 - \frac{3037.5}{T_{SO_2}} - \frac{251586.}{3606.3+T_{SO_2}} + \frac{606003055.}{(3606.3+T_{SO_2})^2}$$

---------(V)

By computation similar to this the relation of CO is found as follows.

$$\log p = 23.05775 - \frac{2091.3}{T_{CO_2}} - \frac{98493.7}{2100.+T_{CO_2}} + \frac{147132427.}{(2100.+T_{CO_2})^2}$$

---------(VI)

(f) $\frac{dp}{dt}$ Expressions for Sulphur Dioxide and Carbon Dioxide

Substituting the values of the constants in the general expression of $\frac{dp}{dt}$, we get

$$\frac{dp}{dt} = 2.3026p\left(\frac{3077.5}{T^2_{SO_2}} + \frac{251586.}{(3606.3 + T_{SO_2})^2} - \frac{606003055.}{(3606.3 + T_{SO_2})^3}\right) \text{---(VII)}$$

for sulphur dioxide, and

$$\frac{dp}{dt} = 2.3026p\left(\frac{2091.3}{T^2_{CO_2}} + \frac{98497.7}{(2100. + T_{CO_2})^2} - \frac{1471[illegible]7.}{(2100. + T_{CO_2})^3}\right) \text{---(VIII)}$$

for carbon dioxide.

These expressions are very important in the Clapeyron equation for specific volume of the vapors.

V. COMPARISONS AND DISCUSSION

(a) Comparisons of Values from Formula with Experimental Data

(1) Of Sulphur Dioxide

Temperature in Deg.Fahr.	Corresponding Pressure in lb per sq. in. of SO_2 from Experiment of Pictet.	Regnault.	Blumcke.	Miller.	Sajotchowski.	from Formul
-4.	8.97					9.20
-1.732		9.69				9.78
32.0	22.2	(22.53 22.64	22.2			22.58
81.04				61.77		61.88
119.84		119.85				120.57
122.0	122.0				123.9	124.34
158.0					210.36	211.15
171.5			251.65			253.19
211.14				416.74		[illegible]
[illegible]					[illegible]	[illegible]

(2) Of Carbon Dioxide

Temperature in Deg.Fahr.	Corresponding Pressure in lb per sq. in. of CO_2 from Experiment of Kuenen & Robson.	Stahli.	Andrew.	Amagat.	Zelnoy.	from Formula
-69.52		75.59				74.44
-69.?3	74.96					74.96
-67.81					78.30	75.59
6.44					340.3	340.63
14.0		379.5				385.10
32.0	504.80					507.62
41.0				573.3		578.27
41.81			591.3			585.15
82.94			1034.5			1002.5
88.43				1071.6		1073.2

The experimental data shown in the preceding tables were taken as the representative points of the experimental results of the different investigators. By representative points is here meant such points as lie fairly well on the curve which represents best the experimental data of a single investigator. The "Pressures from Formula" were computed with the formulas (V) and (VI). It will be seen from preceding tables, to what extent the values from from the formu-

la agree with the observed data of the investigators.

(b) Discussion and Conclusion

Since the experimental data of the different investigators do not agree closely, it is impossible to draw a straight line through all the experimental points plotted on the coordinate system. The straight lines for sulphur dioxide and carbon dioxide on the diagram, however, were laid out so as to represent the most probable pressure-temperature relations of the vapors.

The equation (I) and (II) are the simplest expressions connecting vapor-pressure and temperature. Although, a steam table is indispensible in the computation and also the value of pressure not given on the steam table must be calculated by the straight line relation with nearest given values of pressure, this is the simplest method ever known for the computation of the vapor-pressure corresponding to an assumed temperature; and the results thus obtained are very accurate. (The pressure corresponding to 50.deg.F. computed from the formula (II), was found to be greater by 0.5 pound than that of computed with the formula (VI). This must be due to the difference in in the assumption, that is the difference between the straight line relation and the true curve of saturated steam.)

The general formula (III) or (III') enables one to derive the pressure-temperature equation of any substance when the constants c and k for a pair of that substance and water vapor are known. The general expression of $\frac{dp}{dt}$ (IV) also enables one to derive the $\frac{dp}{dt}$ expression for any particular vapor when the constance c and k for the pair of that substance and water vapor are found.

The equation (V) and (VI) are thought, like Marks' equation

for the pressure-temperature relation of saturated steam, to have advantages over other simple expressions in accuracy of their results. By means of the formula we are able to compute the vapor-pressures of the substance, corresponding to any temperature, without the aid of the steam table. The expressions (VII) and (VIII) are required in the Clpeyron-Clausius formula for the specific volume of the saturated vapors of sulphur dioxide and carbon dioxide.

VI. BIBLIOGRAPHY

(a) Sulphur dioxide

(1) Ramsay and Young: Phil. Mag., v.21 1886 p.33

(2) Traver's Experimental Study of Gasses p.230-9

(3) Moss: Phys. Rev., v.16 1903 p.356

(4) Moss: Phys. Rev., v.25 1907 p.453

(5) Marks: Jan.A.S.M.E., May 1911

(6) Regnault: Mem. de lInt. de France, v. 26 1847 p.581

(7) Sajotchewski: Wiedemann Beiblätter, 3 p.741 1879

(8) Blümcke: Wiedemann Annalen, v.34 p.18 1888

(9) Miller: Jan.A.S.M.E., v.25 1904 p.176

(10) Pictet: O.D.Chwolson, Lehrbuch Der Physik p.729

(11) Dewar: Phil. Mag., ser.5 v.18 p.210 1884

(12) Sajotschewski: Ber.d.d. chem. ges., 11 p.818

(13) Drion: Annales chemie et physique, v.3 56 p.1

(14) Van Ladenburg: Ber.d.d. chem. ges., 11 p.818

(15) Goodenough's Principles of Thermodynamics, p.181

(16) Zeuner'sTechnical Thermodynamics, Part 2 p.236

(17) Peabody' Steam and Entropy Table

(18) Wood: Trans.A.S.M.E. 12 p.137

(19) Faraday: Phil. Trans. 1845 p.155

(20) Cailletet and Mothias: Comptes rendus, v.104 p.1563 1887

(21) Lange: Zeitschrift für Kälteindustric, 1899 p.82

(22) Mathias: Comptes rendus v. 119 p.404 1894

(23) Marks and Davis' Steam Table

(b) Carbon dioxide

(24) Amagat: Comptes rendus, v.114 1892 p.1093

(25) Andrews: O.D.Chwolson, Lehrbuch Der Physik p.729

(26) Cailletet: O.D.Chwolson, Lehrbuch Der Physik p.729

(27) Kuenen and Robson: Phil. Mag., ser.3 p.149 1902

(28) Stähli: Zeit. f.d.ges. Kohlens-Ind., Dec. 1906 p.35

(29) Zelney: Prof.Zelney's letter to Mr.Mosher

(30) Goodenugh's Principles of thermodynamics, p.199

(31) Mosher:

(32) Faraday: Proc. of Roy.Soc. v.24 p.445 1876

(33) Mollier: Zeit.für Kälteindustrie, 1895 pp.66,85

(34) Zeuner'sTechnical Thermodynamics, Part 2 p.262

(35) Regnult: Mem. de L'inst. de France, v.26 1847 p.618

(36) Barns' The Laws of Gasses